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Andrew Guenthner, Kevin R. Lamison, Josiah T. Reams, Vandana Vij, and
Joseph M. Mabry

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Air Force Research Laboratory (AFMC)
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9 Antares Roac
Edwards AFB CA 93524-7401

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Air Force Research Laboratory (AFMC)
AFRL/RZS
5 Pollux Drive
Edwards AFB CA 93524-7048

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14. ABSTRACT
This presentation summarizes the study of the effects of silicon substitution in both network segments (dicyanates) and junctions (tricyanates). It appears that silicon substitution does result in increased free volume, a lower fully cured T_g, and , when compared at the same degree of conversion, lower density, lower packing fraction, and higher coefficient of thermal expansion. In at least some cases, the increased molar volume leads to lower water uptake, apparently by decreasing the overall density of cyanurate groups in the material. Incorporation of silicon in both network segments and at network junctions facilitates attainment of a higher degree of conversion under a given set of cure conditions, and appears to lower the activation energy for cure. This effect can offset or even overcome the effects of increased free volume.

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EFFECTS OF SILICON SUBSTITUTION IN THE MAIN CHAIN NETWORK SEGMENTS OF POLYCYANURATES

28 March 2012

Andrew Guenthner[1]*, Kevin R. Lamison[2], Josiah T. Reams[3], Vandana Vij[2], Joseph M. Mabry[1]

[1]Propulsion Directorate, Air Force Research Laboratory
[2]ERC Incorporated
[3]Air Force Research Laboratory / National Research Council
Ph: 661/275-8020; e-mail: andrew.guenthner@edwards.af.mil

Outline

- Background / Motivation
  - Si Incorporation Enhances Thermo-Oxidation Resistance
  - Other Effects Generally Not Considered
- Effect of Si Substitution on Crystal / Volumetric Properties
- Effect of Si Substitution on Water Uptake
  - Role of Vitreous Cure
  - Dicyanates vs. Tricyanates
- Effect of Si Subsitution on Cure Kinetics
  - Extent of cure vs. Temperature (Late-Stage)
  - Activation Energy

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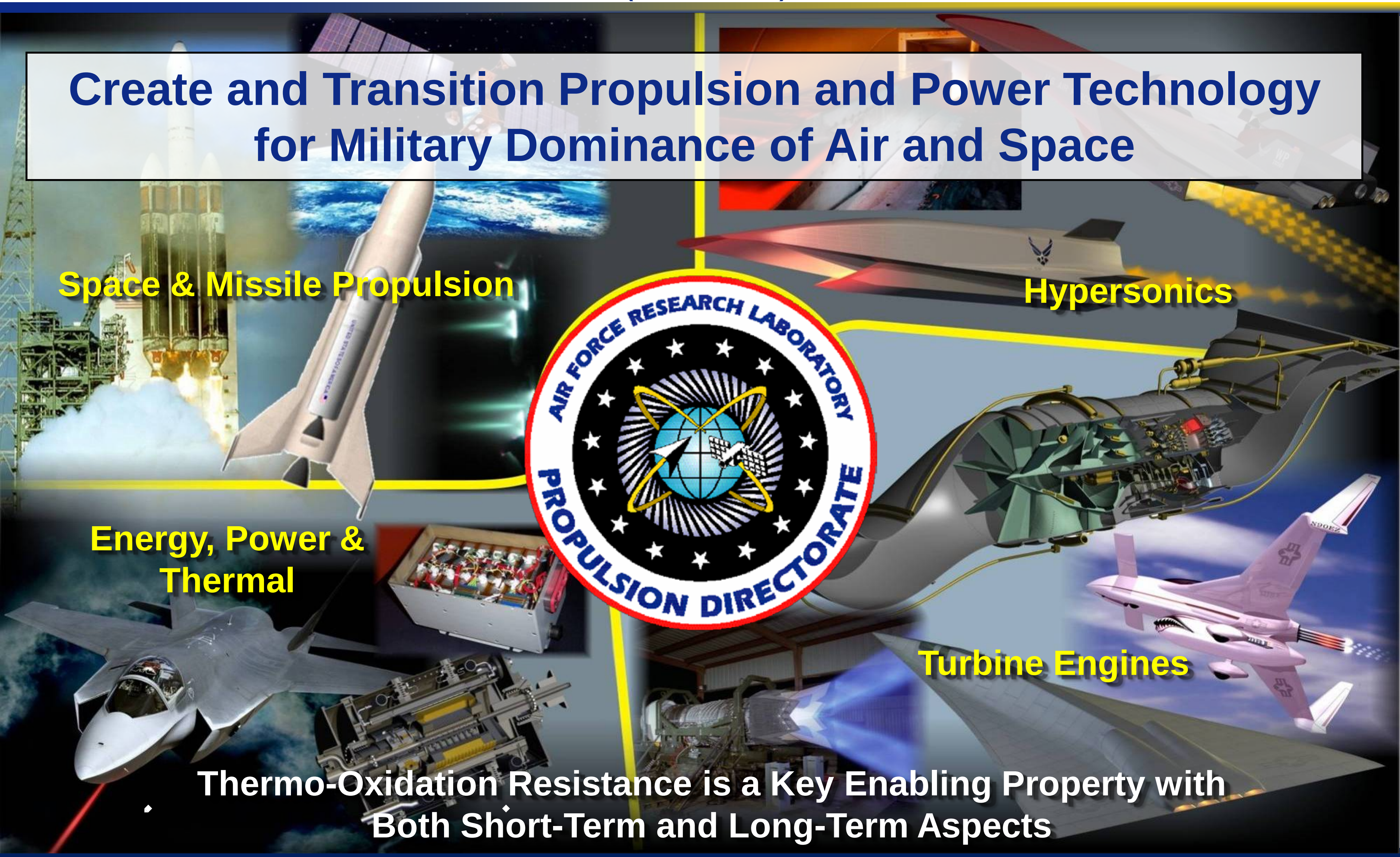
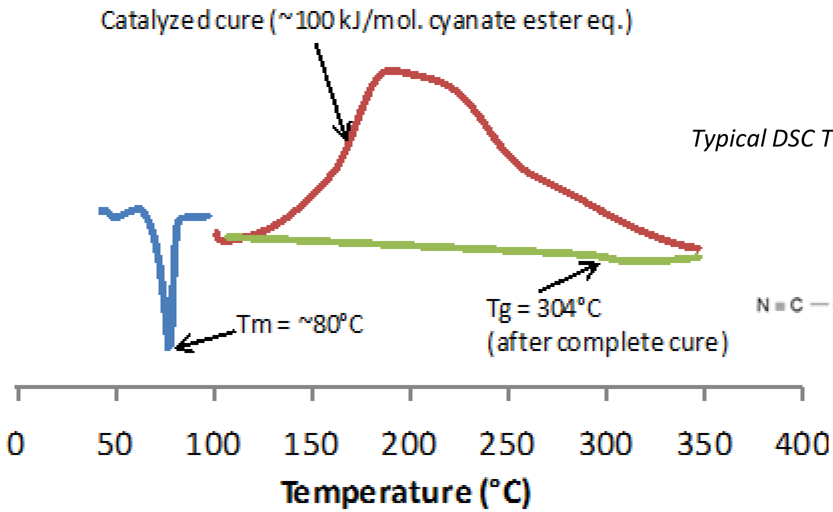
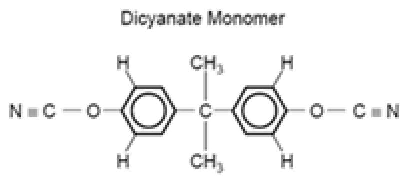


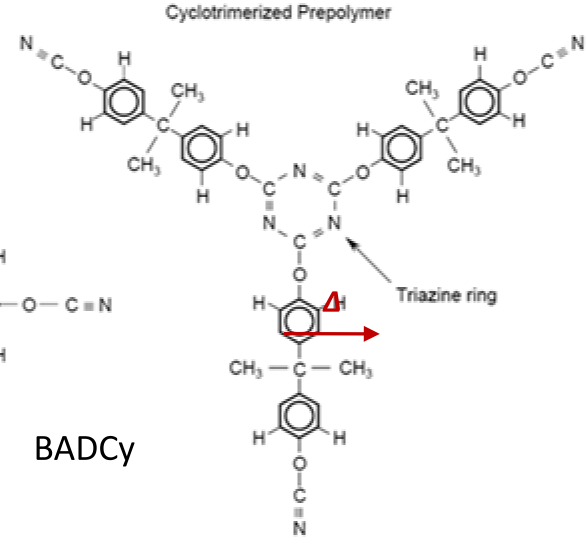
Cyanate Esters: Ideal for Studies of High-Temperature Thermosets



Typical DSC Trace of CEs

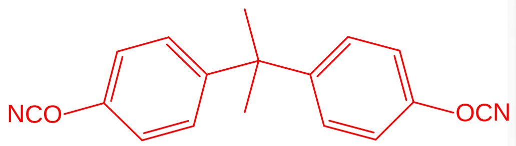


BADCy

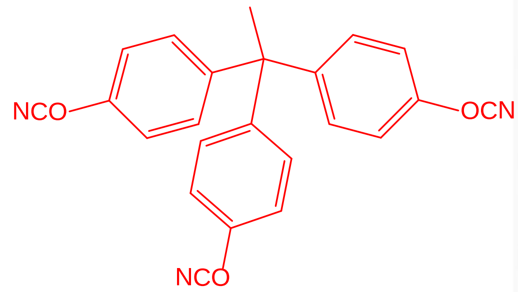


- **Single species reaction chemistry is "cleaner" than epoxy resin and well-understood; enables development of superior predictive models; readily catalyzed to cure at reasonable temperatures, providing a wide and tunable processing window**
- **Amenable to many different composite fabrication processes – filament winding, RTM, VARTM, compression molding, pultrusion; easy to make pure resin samples**
- **Minimal net shrinkage during cure; virtually no volatile released; good flame, smoke, and toxicity characteristics**
- **A wide variety of monomer architectures are available**
- **Highly relevant to propulsion systems, particularly those with short operational lifetimes; used in everything from microelectronics to space probes**

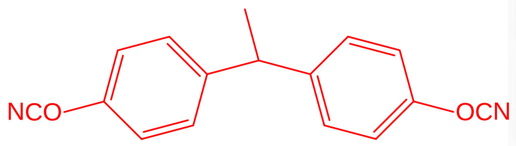
Cyanate Ester Monomers Used



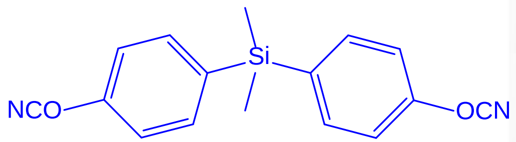
BADCy



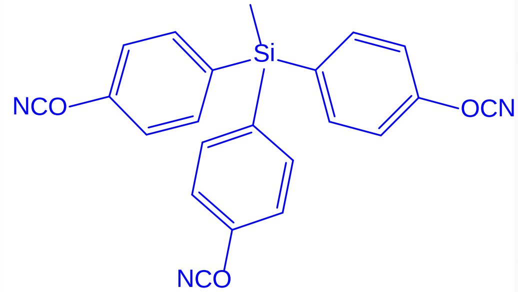
ESR255



LECy



SiMCy



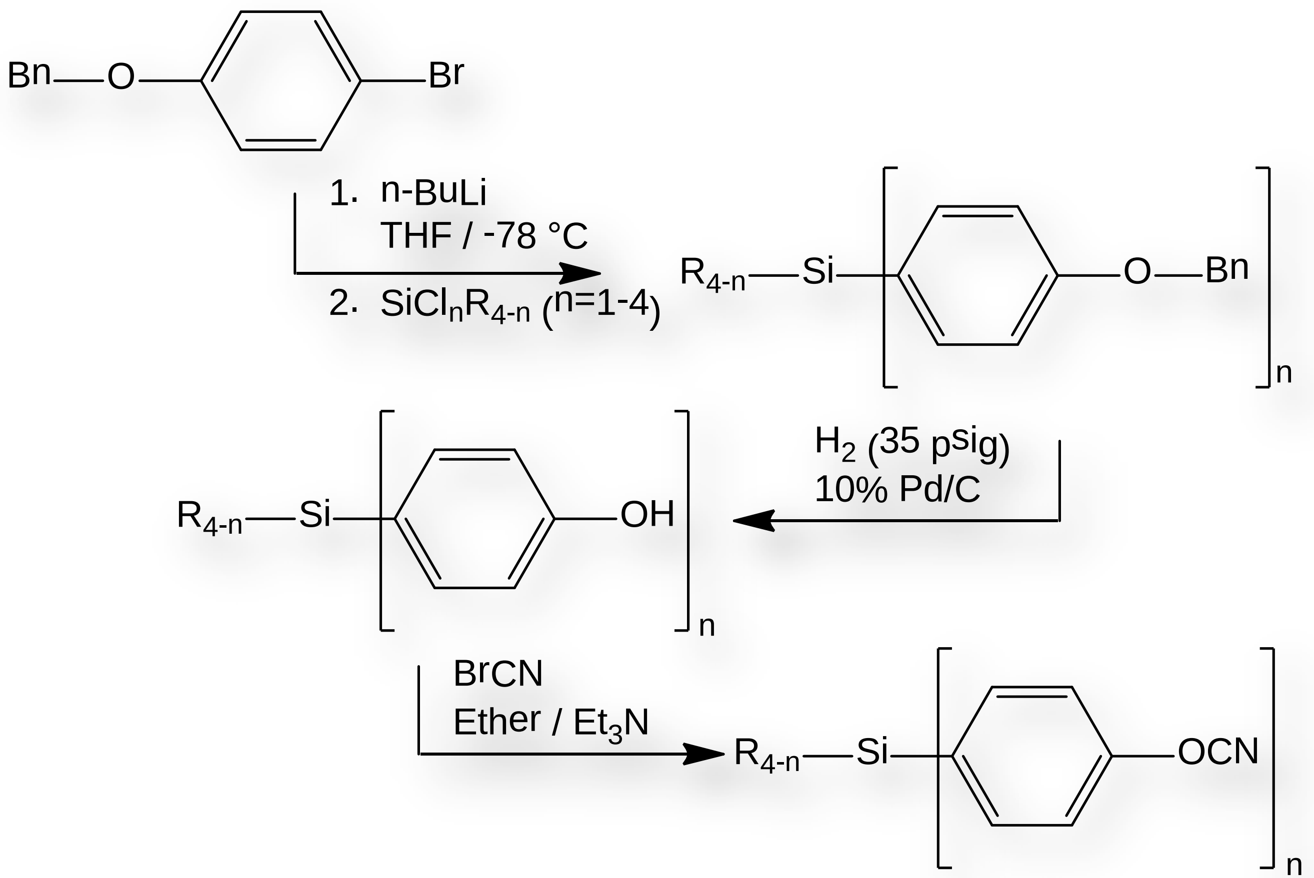
STT3

Catalyzed systems use:

160 ppm Cu(II) as Cu(II)AcAc with 2 phr nonylphenol,

All samples were melted, blended, and de-gassed for 30 min. prior to cure in silicone molds under N_2, cure schedule for 1 hr at 150 °C followed by 24 hrs at 210 °C, with ramp rates at 5 °C / min.

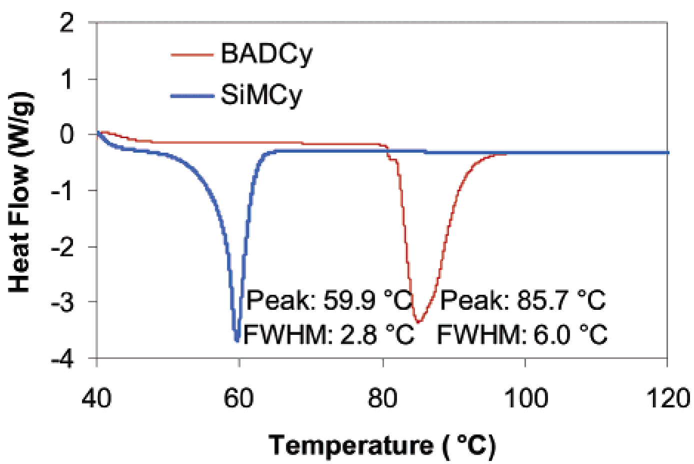
General Synthesis Scheme



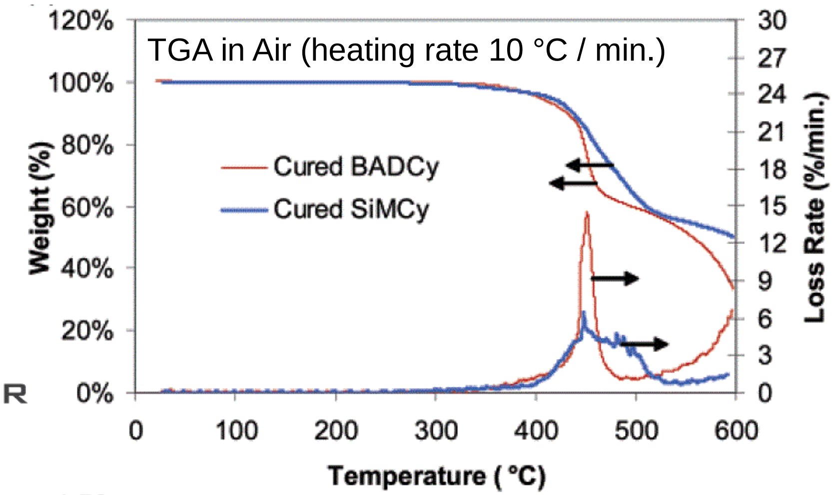
- SiMCy is the n=2 case (Si in network segment), n=3 or n=4 produces Si at network junctions

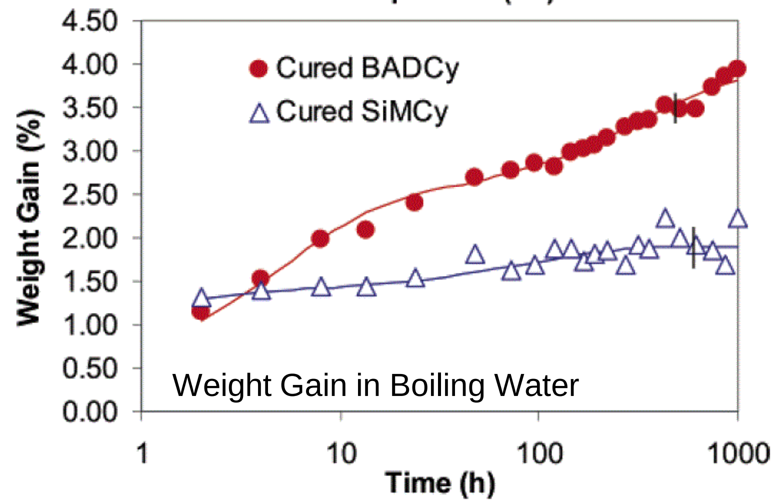
Multiple Effects of Si Substitution Observed in SiMCy

SiMCy, a silicon-containing cyanate ester, was synthesized in 2003 by Dr. Michael Wright at NAWCWD China Lake. Subsequent joint work with AFRL, published in *Macromolecules* (2006) 39, 6046 investigated its moisture uptake properties.



DSC scan of 2,2-cyanatophenylpropane (BADCy) and bis- (4-cyanatophenyl)dimethylsilane 3 (SiMCy) near the melting point.

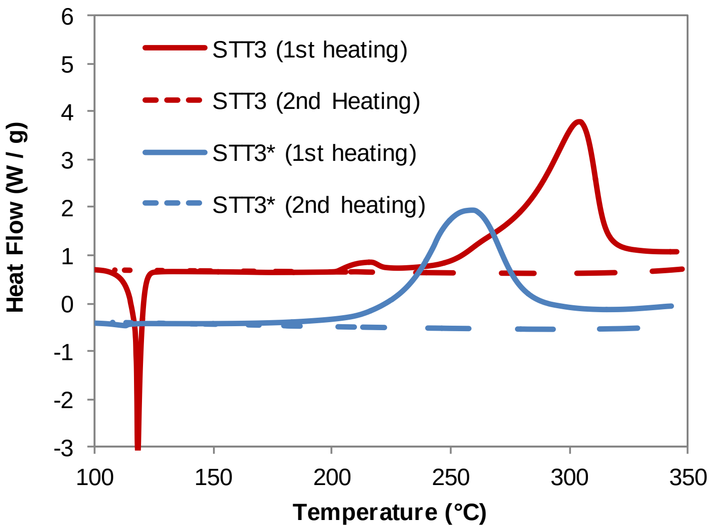




- In addition to the expected increase in short-term thermo-oxidative stability; the substitution of Si also results in lower melting temperatures and lower water uptake

Effect of Si Substitution on Crystal and Network Volumetric Properties

Compound / Property	BADCy	SiMCy	ESR255	STT3
Melting Point, °C (monomer)	79	55	115	118
Density, g/cc @ 20 °C	1.201	1.171	1.270	1.245
Packing Fraction @ 20 °C	0.629	0.617	0.687	0.676
CTE, ppm / °C @ 150 °C	59	70	60	62

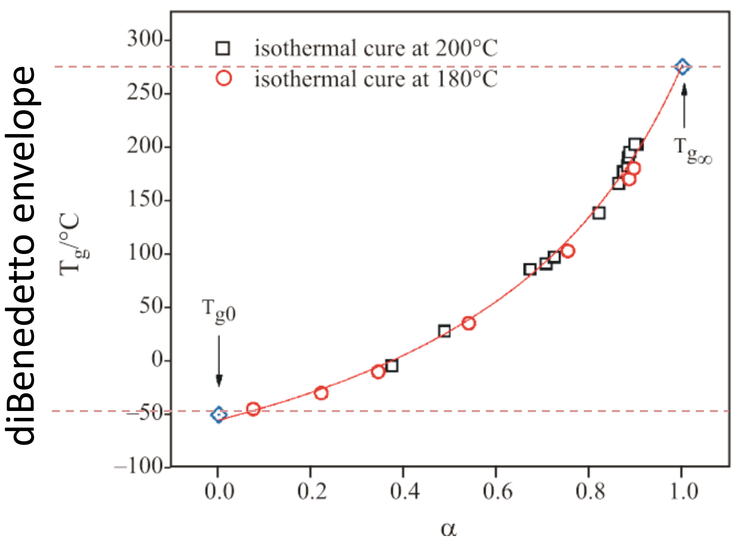


DSC of STT3 monomer (* indicates system catalyzed)

Unless indicated otherwise, properties are for as-cured networks with 85-100% conversion. BADCy and SiMCy systems were catalyzed.

- Incorporation of Si does not consistently lower melting point (likely depends on individual crystal characteristics).
- Incorporation of Si does appear to create free volume and lower network junction density, with a lower fully-cured Tg and higher CTE being the likely result.
- Note that differences in cure can confound these effects to some extent.

Glass Transition vs. Extent of Cure in a Thermosetting Polymer



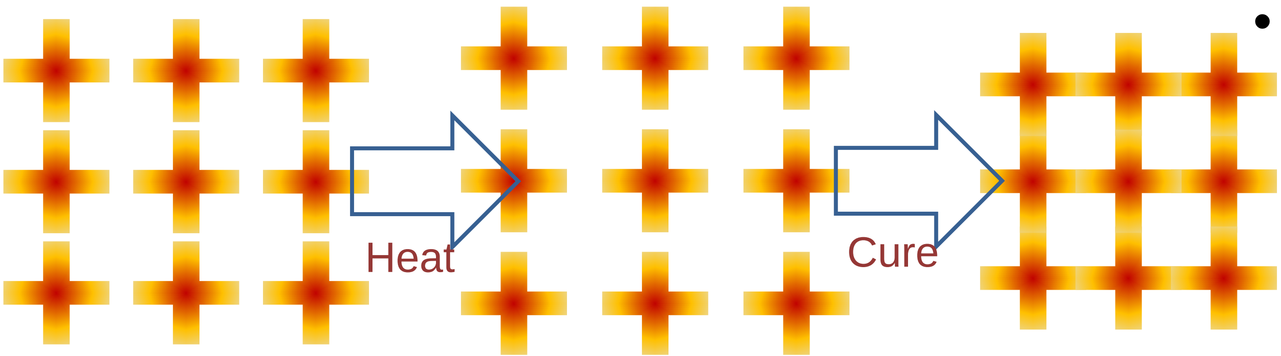
An example of how T_g values can be converted to conversion values based on the diBenedetto equation (from X. Sheng, M. Akinc, and M. R. Kessler, *J. Therm. Anal. Calorim.* 2008, 93, 77-85.) for EX-1510 dicyanate ester resin, for which $T_g << T_{decomp}$

- Note the steep dependence of T_g on conversion as the system reaches full cure
- The need for higher use temperatures pushes up $T_{g\infty}$ as better performing resins are developed
- The need for ease of processing dictates that T_{g0} remain low, preferably below room temperature
- As a result, composite resins are evolving to have an ever steeper diBenedetto curve, which results in a very strong dependence of T_g on conversion.
- Normally, T_g depends on free volume in polymers, but as conversion dependence begins to dominate, the rules for structure-property relationships change

Material °C→	T_{g0}	$T_{g\infty}$	ΔT_g	$dTg/d\alpha\|_{\alpha=1}$
Epoxy	0	150	150	4.5
Polyimide	200	450	250	7.5
Cyanate Ester	-50	300	350	10.5

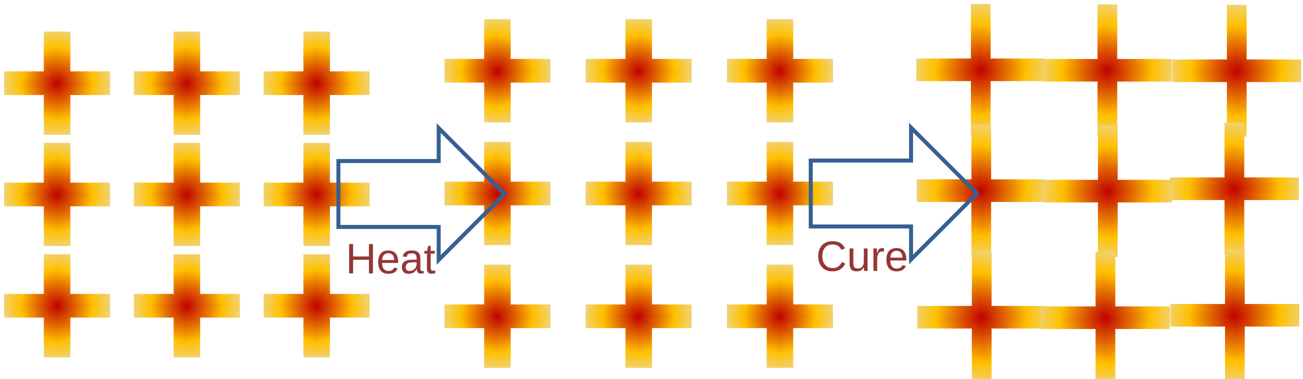
“Vitreous Cure” Differs Markedly from Main Stage Cure

Main Stage Thermal Cure



- Cure results in:
  - *Net Shrinkage*
  - *Less permeability*
  - *Higher modulus*
  - *Brittleness*

“Vitreous Cure”

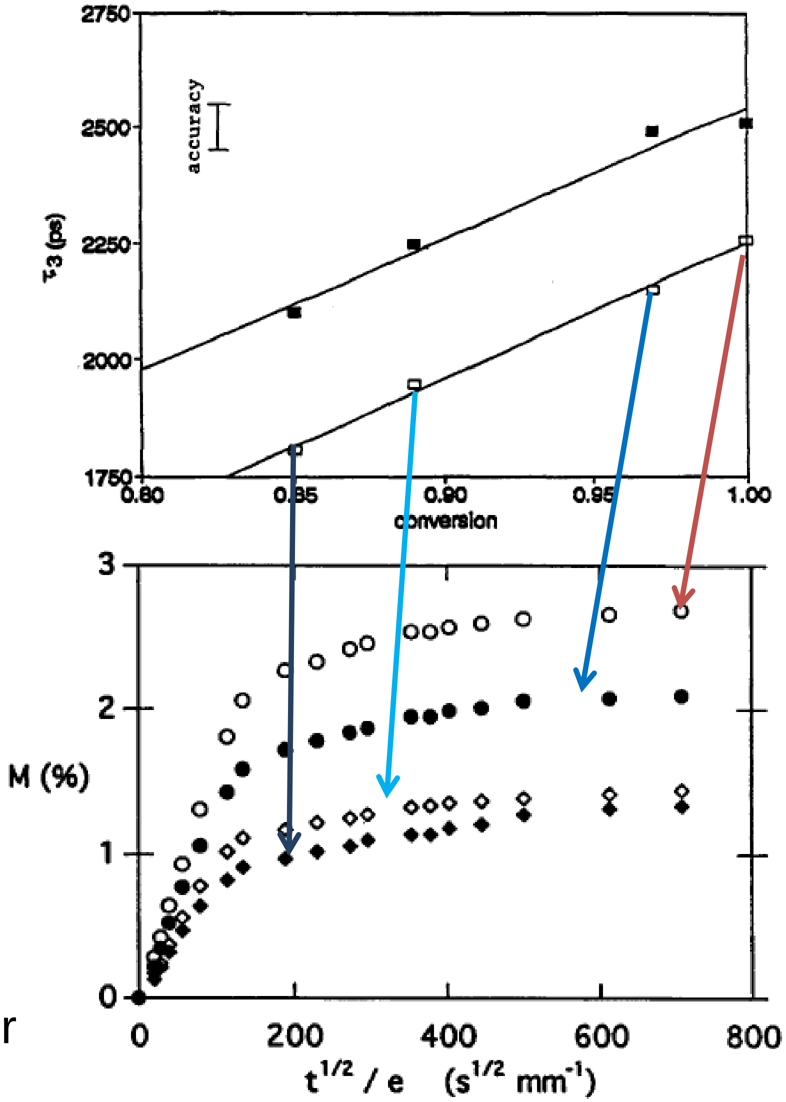


- Cure results in:
  - *Net Expansion*
  - *Higher permeability*
  - *Lower modulus*
  - *Toughness*

- “Vitreous Cure” is promoted by rigid network segments with well-distributed extensibility, and by cure temperatures that are low in comparison to T_g (though $T_{cure} < T_g$ may not be a criterion)
- Both types of cure can happen sequentially, simultaneously, or in mixed form

Water Uptake and Free Volume Associated with Cyanurate Groups

- Georjon and Galy (Polymer 39, 343, 1998) showed that, for BADCy, the late stages of cure led to an increase in free volume associated with the formation of cyanurate groups, and that the formation of free volume was directly connected to increased water uptake.
- Our results to date show:
  - A similar correlation at high conversion for other dicyanate monomers
  - That the effect is limited to very high conversions (at lower conversions, free volume increases but water uptake decreases)
  - Monomers with more free volume overall tend to absorb less water
- Thus, all free volume is not equally useful for water uptake.

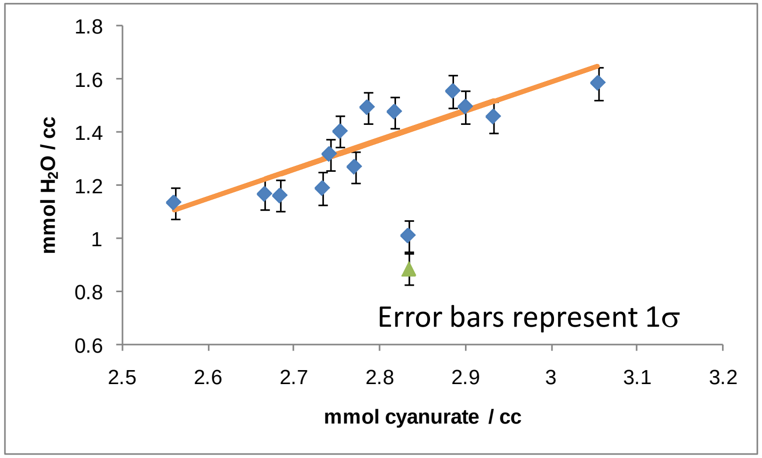


Correlation Between Water Uptake and Cyanurate Density

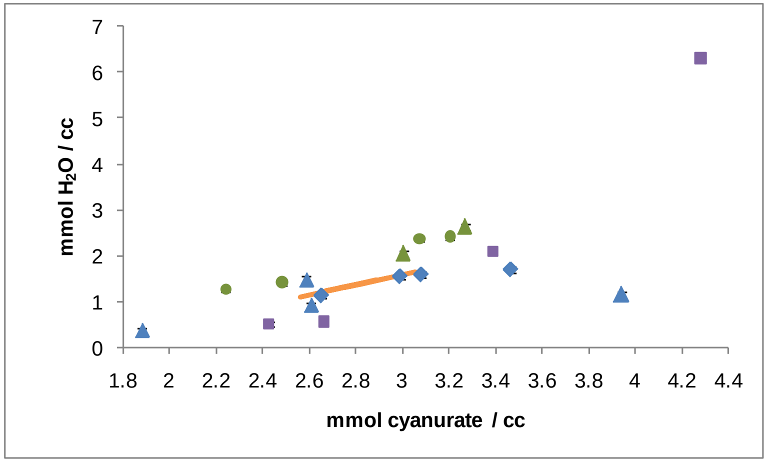
Cyanate Ester - mmol cyanurate/ cc	mmol H_2O / cc
BADCY /3.0	1.7
LECY/ 3.0	1.6
SIMCY / 2.7	1.1
THIOCY / 3.9	1.2
METHYLCY / 2.6	0.9
AroCy F / 2.6	1.5
REX-371 / 3.3	2.6
RTX366 / 1.9	0.4

•Based on data in Appendix a-3 of Hamerton, I (ed)., Chemistry and Technology of Cyanate Ester Resins (Blackie Academic, 1994) (uses monomer density)

In blend samples studied …



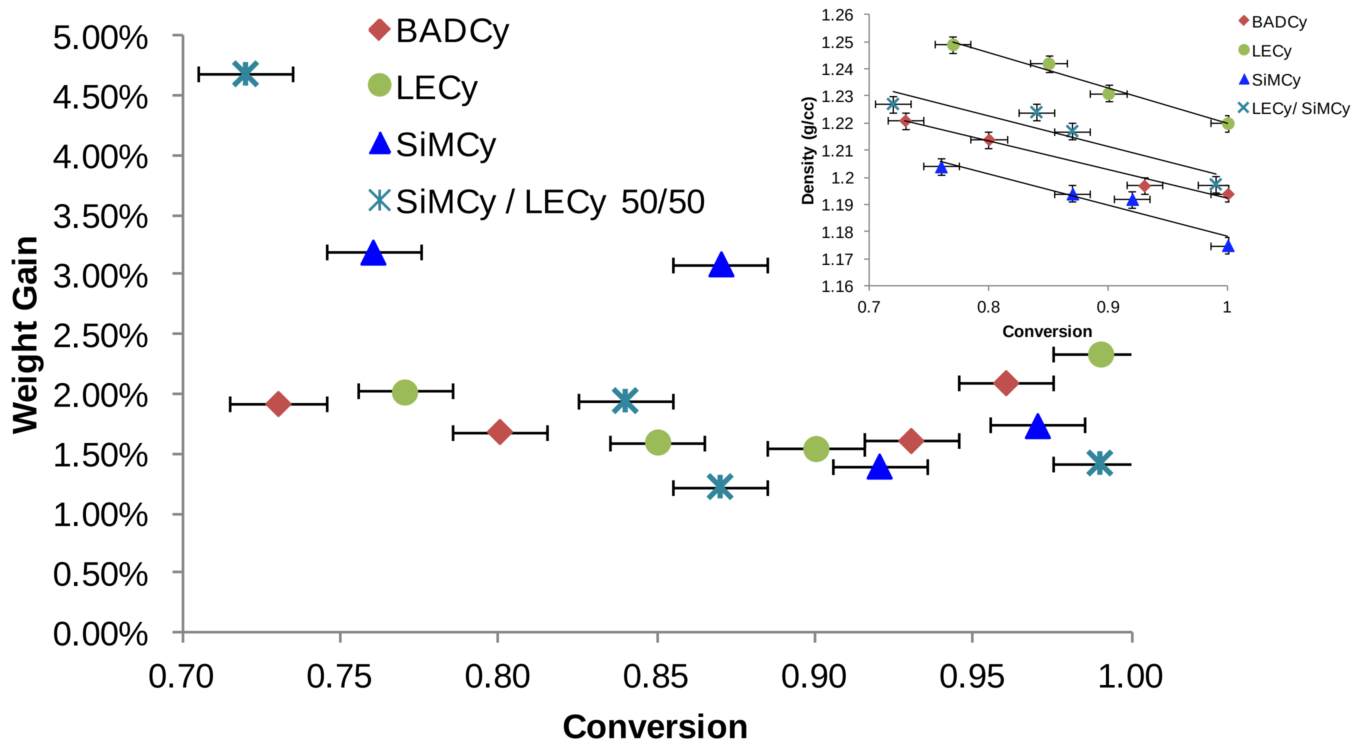
… and over all types of CE resins …



Blue = biphenyl
Green = three-arm
Purple = single-ring (meta)
Orange = blend data
Triangle = lit. value (x-axis uncertain)

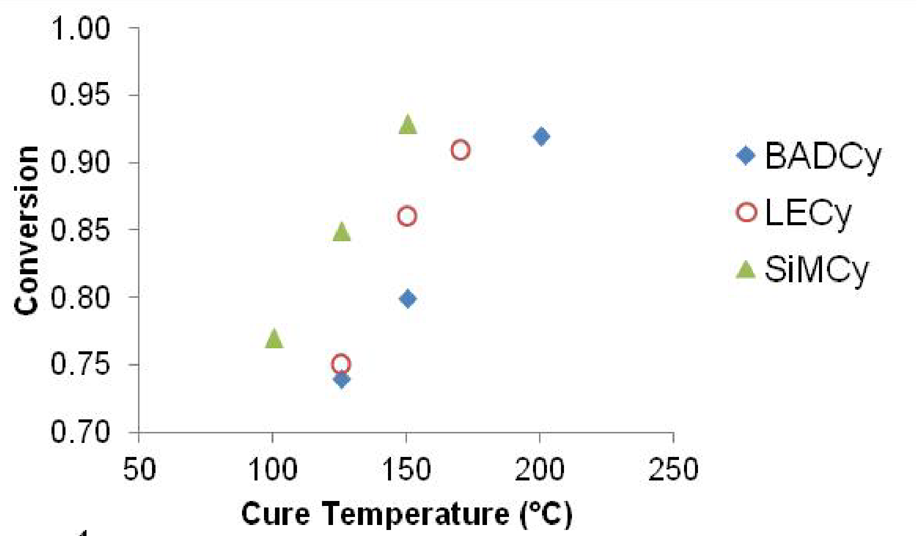
- Maintaining a low density of cyanurate groups appears to limit water uptake

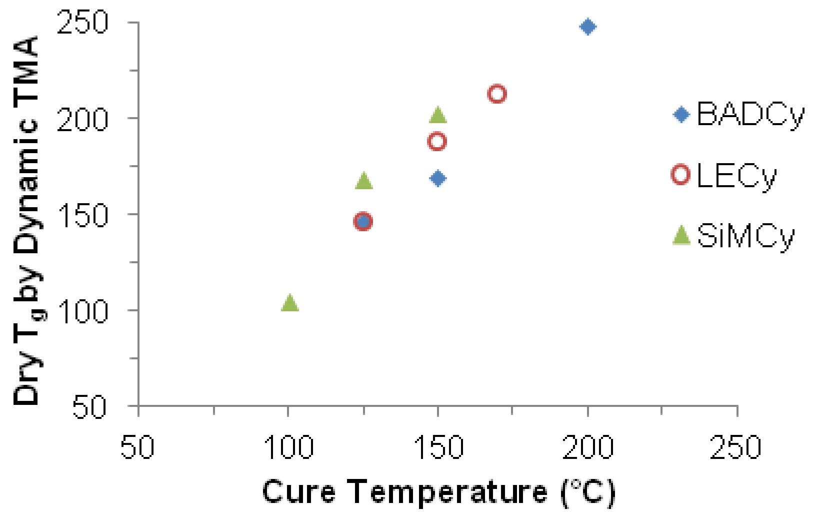
Water Uptake at 96 hrs as a Function of Conversion in Dicyanates

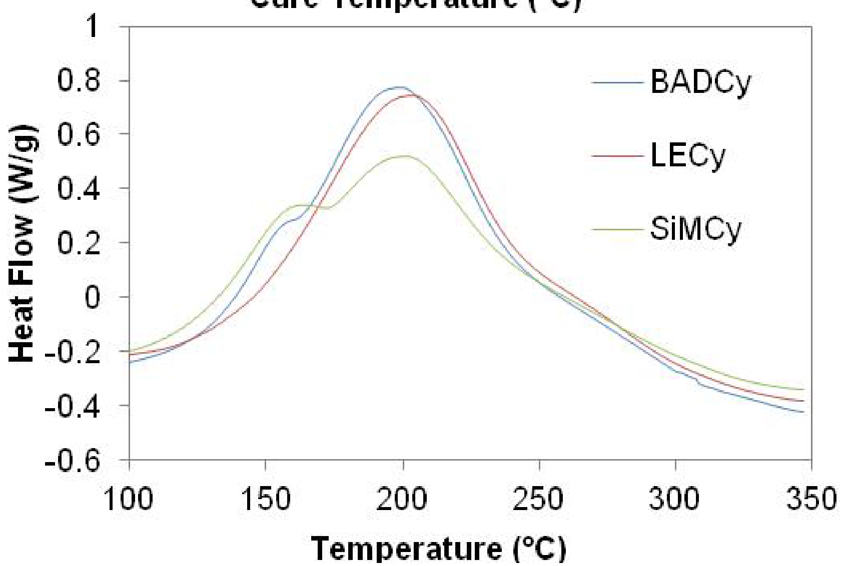


- A comparison of water uptake data (some are interpolations with respect to time) for three dicyanate monomers and one blend shows minima at around 90% conversion, in accord with previous studies of dicyanate esters. The water uptake for fully cured SiMCy is about 25% less than BADCy, while that of the SiMCy / LECy blend is lower than that of either component despite the absence of any unusual features in the density data – a result that has been replicated in three separate trials.

Effect of Si Substitution on Late Stage (Vitreous) Cure



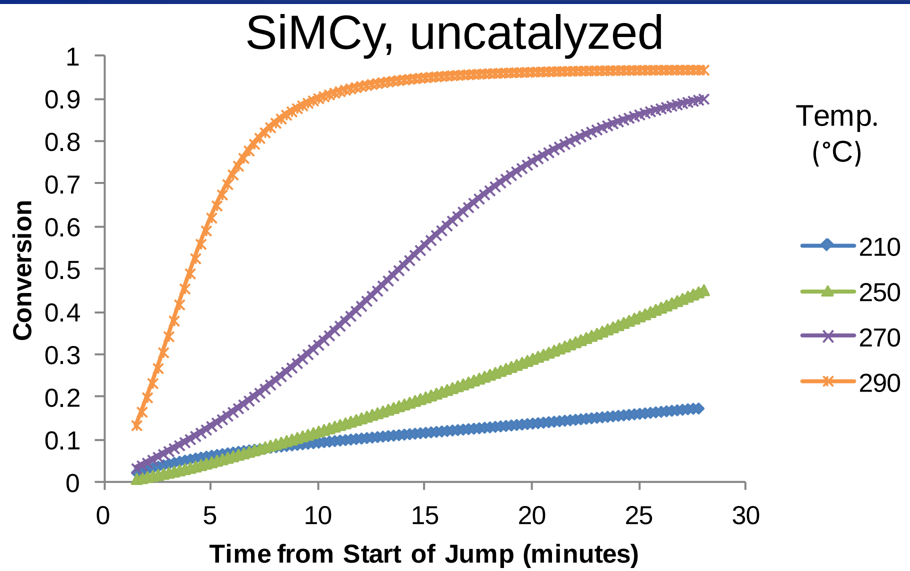


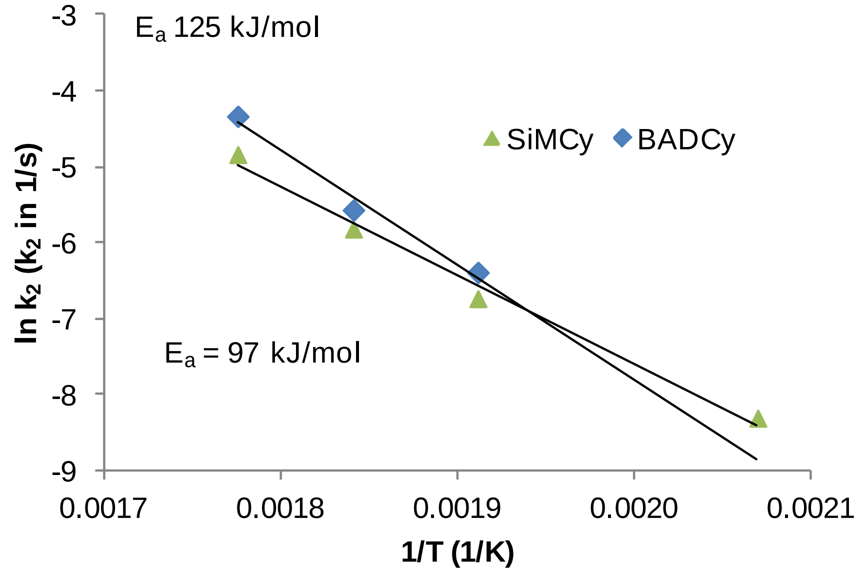


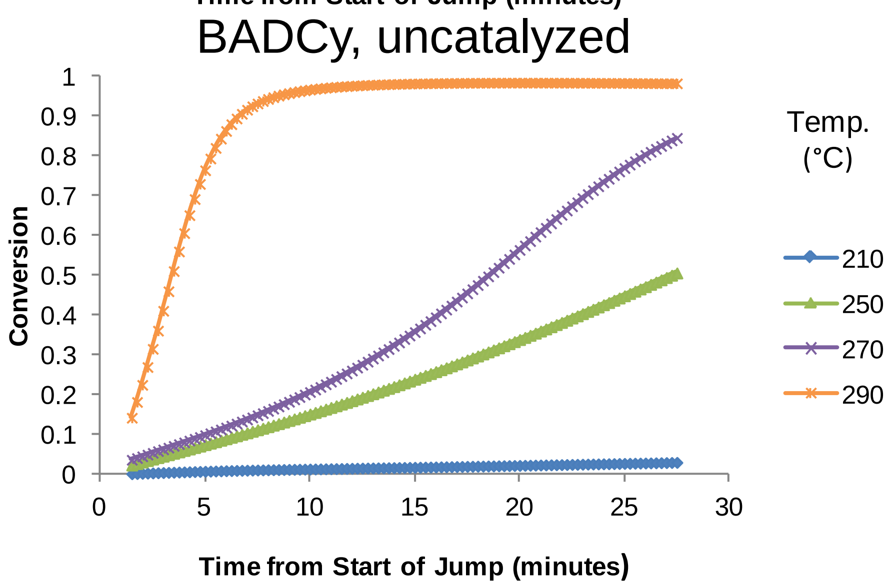
Systems catalyzed with 160 ppm Cu (AcAc) + 2 phr nonylphenol

- SiMCy cures faster and to a greater extent at lower temperatures when catalyzed.
- The relative ease of vitreous cure enables SiMCy to attain a higher T_g for a given cure temperature, despite having the lowest T_g for a given conversion.
- These effects likely caused by flexible core

Effect of Si Substitution on Activation Energy: Dicyanates



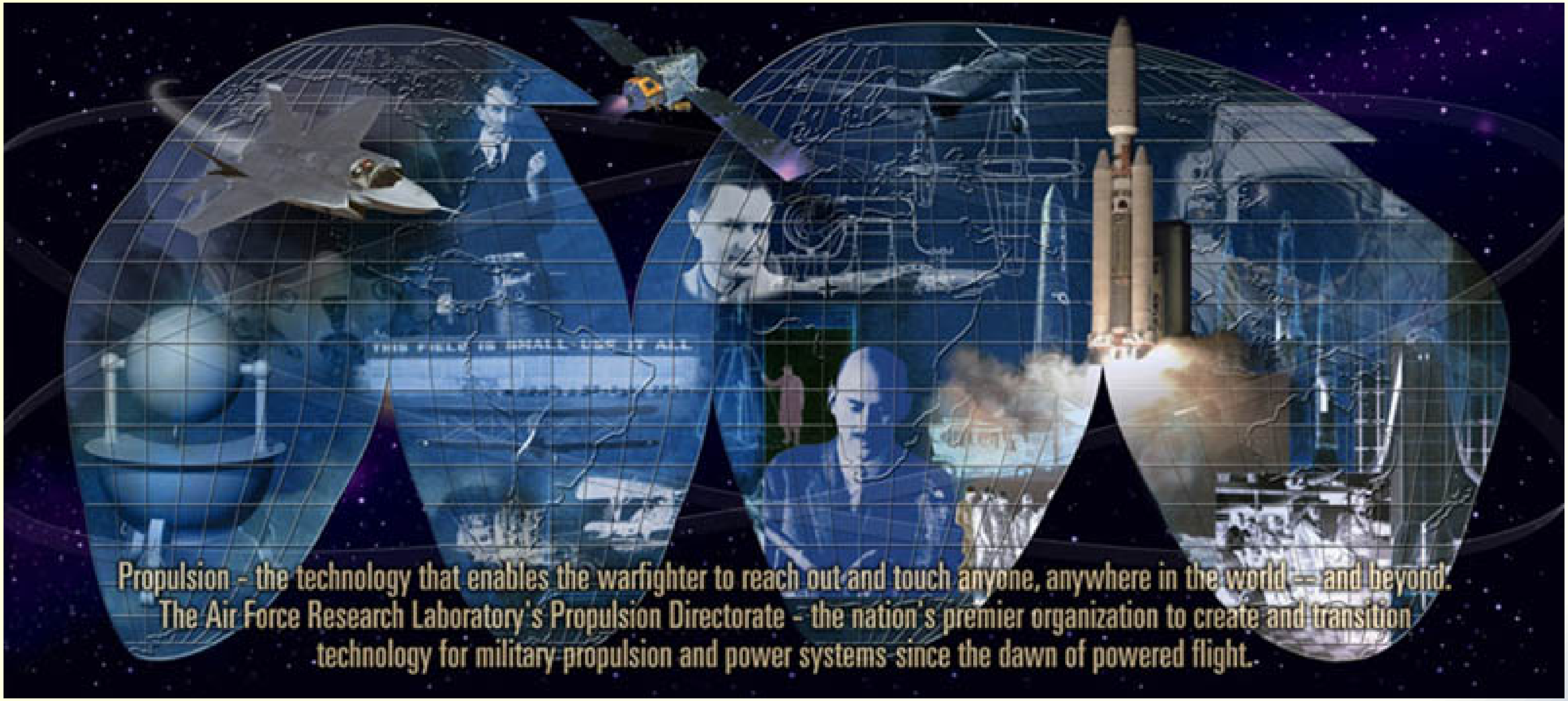




- A more drastic effect of temperature on the conversion vs. time profile of BADCy is evident compared to SiMCy
- In the context of a kinetic model, the result is a lower activation energy for SiMCy
- The lower activation energy is characteristic of a more flexible core.

Summary

- The effects of silicon substitution in both network segments (dicyanates) and junctions (tricyanates) is currently under study.
- It appears that silicon substitution does result in increased free volume, a lower fully cured T_g, and, when compared at the same degree of conversion, lower density, lower packing fraction, and higher coefficient of thermal expansion.
- In at least some cases, the increased molar volume leads to lower water uptake, apparently by decreasing the overall density of cyanurate groups in the material.
- Incorporation of silicon in both network segments and at network junctions facilitates attainment of a higher degree of conversion under a given set of cure conditions, and appears to lower the activation energy for cure. This effect can offset or even overcome the effects of increased free volume.



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